

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



BV

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C09D 5/16		A1	(11) International Publication Number: WO 98/39391 (43) International Publication Date: 11 September 1998 (11.09.98)
(21) International Application Number: PCT/GB98/00706 (22) International Filing Date: 5 March 1998 (05.03.98) (30) Priority Data: 9704794.8 7 March 1997 (07.03.97) GB (71) Applicant (for all designated States except US): <u>COUR- TAULDS COATINGS (HOLDINGS) LIMITED</u> [GB/GB]; 50 George Street, London W1A 2BB (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): HAMILTON, Trevor [GB/GB]; 28 Salisbury Street, Pelaw, Gateshead, Tyne and Wear NE10 0XY (GB). GREEN, Georgina, Elizabeth [GB/GB]; 10 Southfork, Lemington Rise, Newcastle upon Tyne, Tyne and Wear NE15 8TZ (GB). WILLIAMS, David, Neil [GB/GB]; 22A Woolsington Gardens, Woolsington, Newcastle upon Tyne NE13 8AR (GB). (74) Agents: COULSON, Antony, John et al.; Abel & Imray, Northumberland House, 303-306 High Holborn, London WC1V 7LH (GB).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report.	
(54) Title: FOULING INHIBITION			
(57) Abstract <p>A process for inhibiting fouling of a substrate in a foulig environment comprises applying to the substrate, before exposure to teh said environment, a composition which comprises: (A) a polymer carrying pendant and/or terminal curable functional groups, at least a major proportion of the repeating units in the polymer of (A) being other than siloxane units; (B) one or more polysiloxanes having pendant and/or terminal curable functional groups and selected from curable organohydrogen polysiloxanes and curable polydiorganosiloxanes, the curable functional groups in component (B) being capable of undergoing a curing reaction with the curable functional groups in component (A), and curing the applied composition comprising components (A) and (B), if necessary or desired in conjunction with a cross-linking agent, and thereafter applying a layer comprising: (C) a curable organohydrogen polysiloxane or polydiorganosiloxane, and curing the applied layer, if neccessary or desired in conjunction with a cross-linking agent. For enhanced fouling inhibition performance, the curable layer (C) is applied to a freshly-prepared coating formed by curing the composition comprising components (A) and (B). Alternatively, for restoration and/or repair, the curable layer (C) is applied to a coating formed initially by curing the composition comprising components (A) and (B), but which has been worn and/or damaged in use.</p>			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

FOULING INHIBITION

This invention relates to a process for inhibiting fouling of a substrate in a fouling environment, more especially a marine or other aquatic environment.

Man-made structures such as boat hulls, buoys, drilling platforms, oil production rigs and pipes which are immersed in water are prone to fouling by aquatic organisms such as green and brown algae, barnacles, mussels and the like. Marine structures are commonly of metal, but may also comprise other structural materials such as concrete. For smaller boats, the hulls may instead comprise, for example, wood or a fibre-reinforced resin. This fouling is a nuisance on boat hulls, because it increases the frictional resistance towards movement through the water, with the consequence of reduced speeds and increased fuel costs. It is a nuisance on static structures such as the legs of drilling platforms and oil production rigs, firstly because the resistance of thick layers of fouling to waves and currents can cause unpredictable and potentially dangerous stresses in the structure, and, secondly, because fouling makes it difficult to inspect the structure for defects such as stress cracking and corrosion. It is a nuisance in pipes such as cooling water intakes and outlets, because the effective cross-sectional area is reduced by fouling, with the consequence of reduced flow rates.

The commercially most successful methods of inhibiting fouling have involved the use of anti-fouling coatings containing substances toxic to aquatic life, for example tributyltin chloride or cuprous oxide. Such coatings, however, are being regarded with increasing disfavour because of the damaging effects such toxins can have if released into the aquatic environment. There is accordingly a need for non-fouling coatings which do not contain markedly toxic materials.

- 2 -

It has been known for many years, for example, as disclosed in GB 1 307 001 and US 3 702 778 that silicone rubber coatings resist fouling by aquatic organisms. It is believed that such coatings present a surface to which the organisms cannot easily adhere, and they can accordingly be called non-fouling rather than anti-fouling coatings. Silicone rubbers and silicone compounds generally have very low toxic properties. Silicone rubber coatings have, however, gained little commercial acceptance. It is difficult to make them adhere well to the substrate surface that is to be protected, and they are mechanically rather weak and liable to damage.

EP 0 032 597 discloses that silicone polymers onto which organic polymeric segments are grafted may be vulcanised to form non-fouling coatings. The vulcanisation procedure may utilise a crosslinking agent such as tetraethyl orthosilicate and a catalyst such as a tin salt.

GB 2 188 938 discloses that vinylic polymers containing polymeric silicone side chains may be used to form thermoplastic non-fouling coatings.

GB Patent Application 2 192 400 discloses anti-fouling paint compositions which comprise a vinylic copolymer obtained by copolymerisation of:

- (a) 1-50% by weight of a polymerisable unsaturated polysiloxane compound;
- (b) 0-30% by weight of a polymerisable unsaturated alkoxysilane compound; and
- (c) 20-99% by weight of a polymerisable unsaturated vinyl monomer other than (a) or (b).

The disclosed anti-fouling paint compositions may also comprise a hydroxyalkyl-tipped poly(diorganosiloxane) to the extent of 1-50 parts by weight per 100 parts by weight of the vinylic copolymer. The vinylic copolymer and the poly(diorganosiloxane) are not curable one with the other, and the coatings disclosed in GB-A-2 192 400

- 3 -

are thermoplastic and not vulcanised.

Coatings which contain a chemically inert oil or grease, often called a slipping agent, have been reported to offer improved resistance to fouling. GB 1 470 465
5 discloses the use of silicone oils as slipping agents in a vulcanised silicone rubber formulation. GB 1 581 727 discloses the use of silicone-free organic compounds, for example polyolefins with a molecular weight up to about 5000, as slipping agents in a vulcanised silicone rubber
10 formulation.

WO 93/13179 discloses a composition for fouling inhibition which comprises (A) a functional-group containing polymer having no more than a minor proportion of siloxane repeating units and (B) a polysiloxane which
15 is curable with the polymer (A). After application of the composition to a substrate and curing, the innermost region of the resulting coating generally comprises no more than a minor proportion of siloxane material whereas the coating presents a siloxane-rich surface layer to the
20 external environment. As a result, the coating provides fouling inhibition properties whilst at the same time the problems of mechanical weakness of previously proposed silicone rubber coatings are alleviated or avoided. After continued exposure to a fouling environment,
25 however, it has been found that the coating may be worn by fouling attrition to the extent that its fouling inhibition properties are impaired, or there may be physical damage to the coating at any time. There is a need to be able to restore or repair a coating that has
30 been worn or damaged in use.

The present invention provides a process for inhibiting fouling of a substrate in a fouling environment, which comprises applying to the substrate, before exposure to the said environment, a composition which
35 comprises:
(A) a polymer carrying pendant and/or terminal curable

- 4 -

functional groups, at least a major proportion of the repeating units in the polymer of (A) being other than siloxane units, and

(B) one or more polysiloxanes having pendant and/or terminal curable functional groups and selected from curable organohydrogen polysiloxanes and curable polydiorganosiloxanes, the curable functional groups in component (B) being capable of undergoing a curing reaction with the curable functional groups in component (A),

and curing the applied composition comprising components (A) and (B), if necessary or desired in conjunction with a cross-linking agent, and thereafter applying a layer comprising

(C) a curable organohydrogen polysiloxane or polydiorganosiloxane, and curing the applied layer, if necessary or desired in conjunction with a cross-linking agent.

The process of the invention enables the fouling inhibition performance of a coating according to WO 93/13179 to be improved, and also provides a means for restoring or repairing a worn or aged coating of that kind without the expense and difficulty of stripping off the worn or aged material and applying a replacement coating.

Thus, in one form of process according to the invention, the curable layer (C) is applied to a freshly-prepared coating formed by curing the composition comprising components (A) and (B). It is considered that the application of the layer (C) to freshly-prepared coating produces a coating which is less susceptible to the detrimental effects of fouling attrition in use.

The invention also offers the possibility of repairing damaged areas of coating as necessary and of restoring coatings that have been worn through fouling attrition in use. Thus, in another form of process

- 5 -

according to the invention, the curable layer (C) is applied to a coating formed initially by curing the composition comprising components (A) and (B), but which has been worn and/or damaged in use.

5 Restoration of worn coatings may be carried out at any desired intervals, and will typically be carried out on a regular basis. For example, in the case of a coating applied to yachts, restoration may be carried out on an annual seasonal basis or more or less frequently if
10 desired.

The substrate can be any material that is to be used in a fouling, especially aquatic, environment. Thus, for example, the substrate may be metal, for instance, steel or aluminium; wood; concrete; a fibre-
15 reinforced resin such as, for instance, a polyester resin; or another plastics material. A known anti-corrosive coating (such as, for instance, an epoxy, vinyl or alkyd coating) may be applied to the substrate before application of the composition comprising components (A)
20 and (B).

It has been found that a coating formed from a composition comprising components (A) and (B) will in general adhere well to a variety of substrate surfaces without the need to use an adhesion modifier or an
25 intermediate tie-coat. Thus, the coating composition may be applied directly to the surface of the substrate, optionally after a preliminary protective treatment (for example, anti-corrosive treatment in the case of a metal substrate).

30 The invention further provides a substrate bearing a coating which has been applied by the process, i.e., having an outer layer comprising cured component (C).

An especially important aspect of the present invention comprises inhibition of fouling of structures
35 in aquatic and, in particular, marine environments, especially the hulls of boats and ships of all sizes.

- 6 -

The process may also be used more generally, however, in providing, for example, non-stick, easy-clean or anti-graffiti coatings. Examples of such end uses include reduction of bio-fouling or other unwanted deposition in heat exchangers and reduction of deposition of denatured protein material in the production of UHT milk.

When a coating composition comprising components (A) and (B) is applied to a substrate and cured as described, it has been found that the outermost surface region of the resulting coating is relatively rich in siloxane material, whereas the innermost region of the coating is relatively rich in the polymer of component (A), and it is believed that there will generally be a progressive increase in the concentration of siloxane material from the inner to the outer regions of the coating. As a result, the applied coating presents a siloxane-rich surface layer to the external environment and the good non-fouling and other protective properties associated with such material are obtained, but at the same time the mechanical weakness of previously proposed silicone rubber coatings is alleviated or avoided. Typically and advantageously, the siloxane-rich surface layer will be substantially free of unreacted functional groups, which might otherwise provide sites for adherence of fouling organisms.

Expediently, the proportions and nature of components (A) and (B) may lead to visible phase separation in bulk on mixing, or visible phase separation may occur following evaporation of solvent during curing.

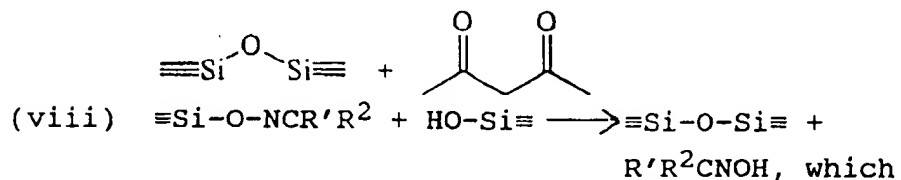
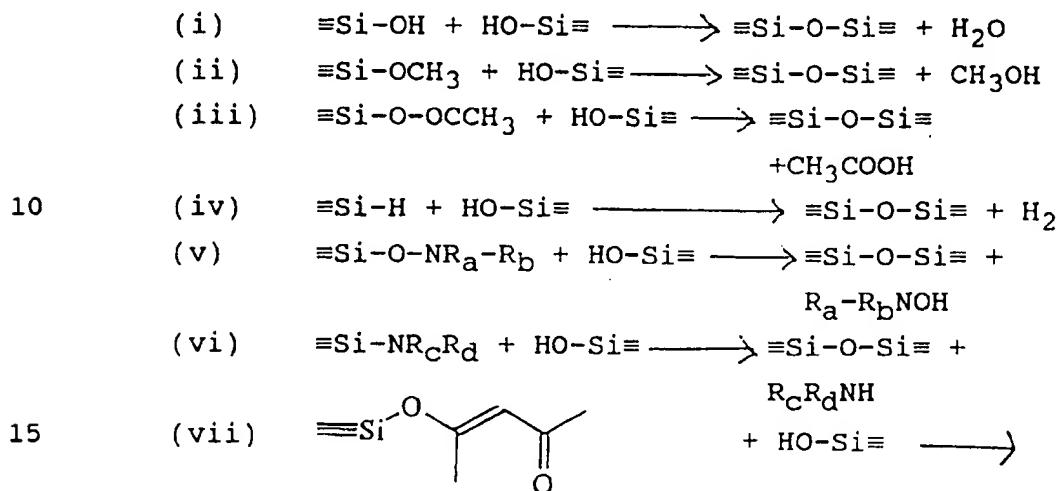
Each of the various curing reactions involved in the process of the invention will in general be a condensation cure which (in the case of curable silicon-containing functional groups) results in the formation of Si-O bonding between the components, and generally in the formation of a by-product corresponding to the curable functional groups participating in the reaction;

- 7 -

other curing reactions, for example, hydrosilation, are possible in principle, but are very much less preferred.

Thus, for example, in the case of curable silicon-containing functional groups, the curing reaction may

5 proceed as follows:



may hydrolyse to an aldehyde or ketone, $\text{R}'\text{R}^2\text{CO}$ and hydroxylamine, NH_2OH , under the conditions of the

20 condensation.

The curing reactions involved in the process of the invention will generally include self-cure of component (B) with itself and, in the case of two or more components (B), will generally include curing of the

25 components (B) together. If there is more than one component (B), it is in principle only necessary for one of them to cure with (A), although in practice the chemistries will typically be such that each component (B) will cure with (A).

30 It may be necessary or desirable to utilise a cross-linking agent for each of the various curing reactions involved in the process of the invention. It will be

appreciated that, in principle, the need or otherwise for the use of such an agent for any given reaction will depend on the functionality and reactivity of the component(s) concerned.

5 Subject to compliance with the (A)/(B) cross-curing criterion specified above, component (A) may comprise curable functional groups selected from epoxy, amino, hydroxy and alkoxy groups and hydrogen atoms, and/or curable silicon-containing functional groups. Advan-
10 tageously, component (A) comprises curable silicon-containing functional groups, and in one form of composition of the invention substantially all of the curable functional groups in component (A) are silicon-containing groups.

15 Component (A) may comprise pendant and/or terminal curable functional groups. Pendant curable functionality is preferred, for example, in the case where the polymer of component (A) is derived from one or more ethyleni-
20 cally unsaturated monomers, and terminal curable functionality is preferred, for example, if the polymer of component (A) is polyurethane, epoxy or polyester based.

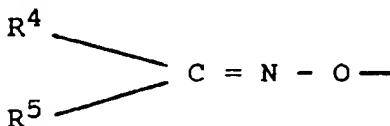
 Preferably, component (A) has di- or tri-functional curable groups, and it is then in general not necessary to provide a separate cross-linking agent for the (A)/(B)
25 curing reaction.

 Although curable silicon-containing groups in component (A) may be silanol groups, the presence of such groups is not necessary and may lead to undesirable curing during storage, and it is certainly preferable for
30 the curable silicon-containing groups to be other than trihydroxysilyl groups.

 Advantageously, curable silicon-containing groups in component (A) are curable by virtue of one or more curable functional groups selected from aliphatic,
35 aromatic and araliphatic ether (for example, alkoxy), ester (for example, acetoxy) and oxime groups. Thus, for

- 9 -

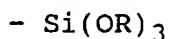
example, curable silicon-containing groups in component (A) comprise one or more oxime groups of the formula



5 in which R^4 and R^5 may be the same or different and each represents a straight-chain or branched, saturated or unsaturated, aliphatic hydrocarbon radical, preferably having up to 7 carbon atoms, more especially up to 4
10 carbon atoms, especially a methyl or ethyl group; an aromatic group, for example, a phenyl group; or an araliphatic group, for example, a benzyl group; or R^4 and R^5 together represent an alkylene group; or one of R^4 and R^5 represents hydrogen. Preferably each of R^4 and R^5 is
15 other than an aromatic group. A group R^4 and/or R^5 may be substituted or unsubstituted.

Curable silicon-containing groups in component (A) may contain more than one curable functional group bonded to silicon, and preferably contain three such groups.

20 Thus, for example, curable silicon-containing groups in component (A) are preferably of the formula



wherein R is a straight-chain or branched alkyl group having from 1 to 4 carbon atoms, preferably a methyl or
25 ethyl group.

Preferably, pendant curable silicon-containing functional groups in component (A) are connected to the polymer by a chemical linkage that is resistant to aqueous hydrolysis in natural waters; sea water, for
30 example, has pH 8.0-8.3. The silicon-containing bonds which are capable of undergoing condensation curing as described above, for example silyl ether and silyl ester, are therefore generally unsuitable for the purpose of attaching silicon-containing groups to the polymer back-
35 bone. It is preferred that the said chemical linkage should contain silicon directly linked to carbon. For

example, the chemical linkage may comprise an alkylene group C_nH_{2n} where n is a non-zero integer preferably having the value 1-5, an alkylidene group, or an arylene group, for example phenylene, or may be a direct chemical bond to a carbon atom in the polymer backbone.

Advantageously, the polymer of (A) is derived from one or more monomers (A1) which carry curable silicon-containing groups and one or more monomers (A2) which do not carry such groups. In the case of monomer(s) (A) carrying pendant curable silicon-containing groups, the molar proportion of monomer(s) (A1) to that of monomer(s) (A2) may be in the range of from 1% to 30% or 50%, for example from 5% to 16%, advantageously from 5% to 14%, preferably from 5% to 12%, and more especially from 5% to 10% or from 1% to 5%.

Polymers (A) carrying curable silicon-containing groups may expediently be manufactured by the polymerisation of one or more monomers containing such groups, advantageously with one or more comonomers which do not contain such groups. For example, such silicon-containing monomers may be derivatives of compounds such as acrylic acid, methacrylic acid, styrene, or ethylene. Examples of derivatives of acrylic and methacrylic acid are the esters in which the esterifying group includes the said silicon-containing group. As particular examples of such derivatives there may be mentioned 3-(trimethoxysilyl)propyl acrylate and methacrylate (I) and 3-(dimethyl(trimethoxysilyloxy)silyl)propyl acrylate and methacrylate (II) (Me represents \equiv methyl).

$CH_2=CRCO_2(CH_2)_3Si(OMe)_3$ (I) R represents H or CH_3

$CH_2=CRCO_2(CH_2)_3SiMe_2OSi(OMe)_3$ (II) R represents H or CH_3

Compound I(R represents CH_3) is particularly preferred.

Examples of derivatives of styrene as monomers (A1) are those in which a benzene ring is substituted both

- 11 -

with a vinyl or 2-propenyl group and with a silicon-containing group. As particular examples of styrene derivatives there may be mentioned the isomeric trimethoxysilylstyrenes and the isomeric 2-(trimethoxysilyl-ethyl)styrenes. As examples of derivatives of ethylene as monomers (A1) may be mentioned trimethoxyvinylsilane and triethoxyvinylsilane.

Instead of using monomers (A1) which already carry curable silicon-containing groups, it is possible (but less preferred) to graft such groups, for example trimethoxysilyl groups, onto a preformed polymer carrying suitable reactive sites at which the curable silicon-containing groups can be attached.

The polymer of component (A) may be derived from one or more ethylenically unsaturated monomers, more especially from one or more ethylenically unsaturated monomers selected from unsaturated aliphatic hydrocarbons, for example, ethylene, propylene and butylene; unsaturated halogenated hydrocarbons, for example, vinyl chloride, vinyl fluoride, vinylidene chloride and vinylidene fluoride; vinyl aromatic compounds, for example, vinyl pyridine, vinyl naphthalene, and styrene (including ring-substituted styrenes); unsaturated acids, esters, amides and nitriles; and N-vinyl compounds, for example, N-vinyl pyrrolidone, N-vinyl carbazole and N-vinyl caprolactam. Mention should also be made of polyvinylacetate and polyvinylalcohol.

As further possibilities, the polymer of component (A) may comprise repeating units derived from urethanes, ureas, urethane-ureas, amides, imides, amide-imides, epoxy compounds, and esters. Mention should also be made of alkyl resins and polyethers.

As particular examples of olefinic monomers may be mentioned such compounds as acrylic and methacrylic acids and their ester, amide and nitrile derivatives, styrene and vinyl chloride. Acrylate and methacrylate

- 12 -

esters are preferred monomers, especially those derived from saturated alcohols containing 4-16 carbon atoms, such as the butyl, hexyl, octyl, decyl, dodecyl and hexadecyl esters. It may also be advantageous to

5 incorporate one or more monomers with reactive functionality to promote adhesion to the underlying surface, for example epoxy functionality derived, for instance, from glycidyl acrylate or methacrylate, or amino functionality derived, for instance, from an aminoalkyl acrylate or

10 methacrylate such as dimethylaminoethyl methacrylate.

It is generally advantageous on grounds of cost, and also to avoid excessive curing, to minimise the proportion of monomers (A1) carrying pendant curable silicon-containing groups in the polymer (A).

15 In a preferred embodiment, the polymer (A) comprises 1-40 mole% 3-(trimethoxy-silyl)propyl methacrylate (TMSPM) and 60-99 mole% dodecyl methacrylate (lauryl methacrylate).

It may also be advantageous to utilise two or more

20 different comonomers not containing a curable silicon group, for example a C₁₋₄ alkyl acrylate or methacrylate ester together with a C₆₋₁₆ acrylic or methacrylic ester. Thus, for example, in another preferred embodiment, polymer (A) is derived from the following monomers in

25 the following molar proportions:

TMSPM		5%
Lauryl or butyl acrylate	40%)	
)	95%
Methyl methacrylate	60%)	

30 Although the polymer of component (A) may include a proportion of siloxane repeating units, at least a major proportion of the repeating units, and preferably at least 55% of the units, are other than siloxane units. The proportion of siloxane repeating units is advantageously not more than 25%, preferably not more than 10%,

35 and more especially not more than 5%. In a preferred form of composition, the polymer of component (A) is

substantially free of siloxane repeating units.

Polymer (A) may have a number-average molecular weight in the range of from 1000 to 50000, preferably from 5000 to 20000, advantageously from 5000 to 15000
5 more especially from 3000 to 15000.

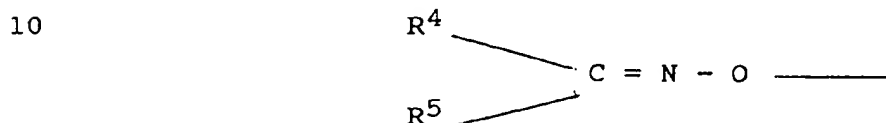
If appropriate, a chain transfer agent may be used in the production of the polymer of component (A). As examples of chain transfer agents there may be mentioned 1-dodecanethiol and mercaptopropyltrimethoxysilane. The
10 molecular weight of the polymer may also be controlled by varying the content of polymerisation initiator. Examples of preferred free-radical initiators include organic peroxides such as tert-butyl peroxy-2-ethyl-hexanoate (available under the trade name Trigonox 215)
15 and the materials available under the trade names Trigonox 27 and Trigonox 41-C 75.

The or each polysiloxane of component (B) in a composition according to the invention may be an organohydrogenpolysiloxane or a polydiorganosiloxane.
20 The polysiloxane may, for example, comprise a copolymer of diorganosiloxane units with organohydrogen siloxane units and/or with other diorganosiloxane units, or a homopolymer of organohydrogen siloxane units or of diorganosiloxane units.

25 Subject to compliance with the (A)/(B) cross-curing criterion specified above, as well as any (B) self-curing criterion, a curable polysiloxane(s) of the present invention (B) may in principle contain any of the functional groups, which may be pendant and/or terminal,
30 described above in connection with component (A) as susceptible to polysiloxane curing. There are not the same disadvantages, however, arising from the presence of silanol groups in component (B) as in component (A), and component (B) is advantageously curable by virtue of such
35 groups. Additionally or alternatively, component (B) may be curable by virtue of curable functional groups

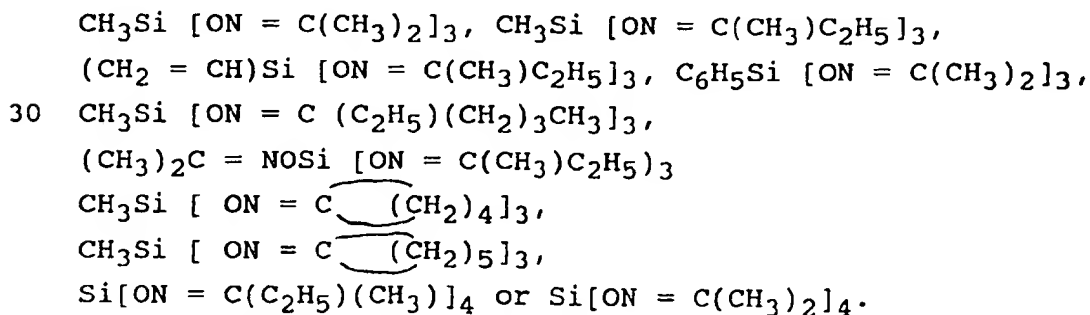
selected from aliphatic, aromatic and araliphatic ether, ester and oxime groups, which may be substituted or unsubstituted, or also trialkoxysilyl or hydrosilyl groups. A curable ether group may be, for example, an alkoxy group such as, for instance, methoxy or ethoxy. An example of a curable ester group is acetoxo.

Thus, by way of preferred example, a curable polysiloxane (B) may be curable by virtue of oxime groups of the formula



in which R^4 and R^5 may be the same or different and each represents a straight-chain or branched, saturated or unsaturated, aliphatic hydrocarbon radical, preferably having up to 7 carbon atoms, more especially up to 4 carbon atoms, especially a methyl or ethyl group; an aromatic group, for example, a phenyl group; or an araliphatic group, for example, a benzyl group, or R^4 and R^5 together represent an alkylene group, or one of R^4 and R^5 represents hydrogen. A group R^4 and/or R^5 may be substituted or unsubstituted.

Oxime-functional polysiloxanes may be prepared by reaction of the corresponding hydroxy-functional siloxane with a ketiminoxysilane, for example, methyl tris(methyl-ethylketiminoxysilane), or one or more of the following ketiminoxysilanes:



Preferred components (B) are linear polymers and advantageously have the structure $\text{R}^3\text{O}(\text{SiR}^1\text{R}^2\text{O})_n\text{R}^3$,

- 15 -

in which R^1 and R^2 , which may be the same or different on each silicon atom and on different silicon atoms in the polymer, each represents an alkyl group such as, for example, methyl, ethyl, or propyl; an alkenyl group such as, for example, vinyl or allyl; a cycloalkyl or cyclo-
5 alkenyl group; an aryl group such as, for example, phenyl; or a halogenated or cyano-substituted hydrocarbon group, with the proviso that one of R^1 and R^2 may represent hydrogen on some or all of the silicon atoms and
10 that R^1 and R^2 may each represent hydrogen on some of the silicon atoms,

OR³ represents a curable functional group in which R^3 represents a monovalent radical such as, for example, hydrogen, alkyl, aryl or R^4R^5CN where R^4 and R^5 are as
15 hereinbefore defined, and

n represents a degree of polymerisation. Preferably R^1 and R^2 are each methyl, although partial or total replacement of R^2 by phenyl may be of advantage.

Although component (B) may in principle be curable
20 by virtue of amino groups, preferred component(s) (B) do not include any amino functionality.

It is generally advantageous for at least some and preferably all curable functional groups in component (B) to be bonded directly to silicon.

25 The polysiloxane component (B) may have a number-average molecular weight in the range of from 1500 to 310 000, generally from 1800 to 80 000 or 85 000. Preferably, the number-average molecular weight of component (B) is at least 5000, advantageously at least
30 10 000, and more especially at least 15 000. The upper limit of molecular weight will usually be 60 000 or 70 000.

The polysiloxane component (B) preferably has a viscosity in the range of from 7.5 to 200 poise at 25°C.
35 By way of illustration, it will in general be desirable to utilise a hydroxy-functional polysiloxane having a

- 16 -

viscosity towards the upper end of the range, whereas for an oxime-functional polysiloxane it will in general be desirable to utilise a material having a viscosity towards the lower end of the range.

5 Advantageously, in a composition comprising components (A) and (B), the proportion of component (A) is in the range of from 50 to 99% by weight, preferably from 84 to 98% by weight, more especially from 90 to 98% by weight, and the proportion of component (B) is in the
10 range of from 1 to 50% by weight, preferably from 2 to 16% by weight, more especially from 5 to 16% by weight, in particular from 2 to 10% by weight, all percentages being based on the total weight of (A) + (B).

 In a preferred form of composition, the proportion
15 of component (B) is at least 5% by weight, advantageously at least 10% by weight, and more especially from 10 to 25 or 30% by weight, all percentages being based on the total weight of (A) + (B).

 A composition comprising components (A) and (B) may
20 include a curing catalyst, especially for condensation cure, and in general will include such a catalyst. Examples of catalysts which may be used include amines and the carboxylic acid salts of various metals, for example, tin, zinc, iron, lead, barium and zirconium.
25 The salts are preferably salts of long-chain carboxylic acids, for example, dibutyltin dilaurate, dibutyltin dioctoate, iron stearate, tin (II) octoate and lead octoate. Further examples of suitable catalysts include
30 organobismuth and organotitanium compounds and organo-phosphates such as bis(2-ethyl hexyl) hydrogen phosphate.

 Other possible catalysts include chelates such as, for example, dibutyltin acetoacetate.

 As a further possibility, the catalyst may comprise a halogenated organic acid, which has at least one
35 halogen substituent on a carbon atom which is in α -position relative to the acid group, and/or at least one

halogen substituent on a carbon atom which is in β -position relative to the acid group, or a derivative which is hydrolysable to form such an acid under the conditions of the condensation reaction.

- 5 Where appropriate in the following description, references to the acid catalyst include references to hydrolysable derivatives thereof.

The acid catalyst may be a mono-, di- or polybasic acid, but is preferably a monobasic acid.

- 10 The acid catalyst is a protonic acid and may comprise one or more carboxylic and/or sulphonic acid groups, preferably one or more carboxylic acid groups.

The or each halogen substituent may be fluorine, chlorine or bromine, but is preferably chlorine.

- 15 Advantageously, on an α - and/or a β -carbon atom of the acid catalyst, there are one or two fluorine substituents, from one to three chlorine substituents, or three bromine substituents. Thus, for example, the acid catalyst may comprise dichloroacetic acid, trichloro-
20 acetic acid or tribromoacetic acid.

- There are preferably one or more halogen substituents on a carbon atom which is α - to the acid group, but if there is no halogen substituent on the α -carbon there will preferably be one or more other functional
25 groups, for example hydroxy or oxo, on that carbon atom and one or more halogen substituents on the β -carbon. Thus, for example, the catalyst may comprise 3-dichloro-2-dihydroxy propanoic acid, or 3-trichloro-2-dihydroxy-propanoic acid.

- 30 The acid is advantageously an aliphatic acid, but may comprise one or more aromatic groups, such as phenyl or substituted phenyl, provided that there is preferably no aromatic group attached to the α -carbon atom or bonded directly to the acid group. An aromatic group may be a
35 heterocyclic group, such as pyridyl or pyrrolyl. An aliphatic acid may be a cyclic or, preferably, an acyclic

acid.

Advantageously, the catalyst is a halogenated alkanolic acid having up to 5 carbon atoms or a hydroxy-substituted derivative of such an acid.

5 As examples of acid derivatives which are hydrolysable to form the acids under the conditions of the condensation reaction there may be mentioned anhydrides, for instance, trichloroacetic acid anhydride, and esters, which may be hydrocarbyl esters, especially methyl esters,
10 or alkyl silyl esters, advantageously C₁₋₄ alkylsilyl esters, especially methylsilyl esters. Thus, for example, the catalyst may comprise trimethylsilyl-trichloroacetate.

If the catalyst contains more than one acid group,
15 there may be halogen substitution on each α - and/or β -carbon atom or on only some of those carbon atoms.

The acid catalyst may carry one or more other substituents in addition to the specified halogen substitution.

20 The acid catalyst may be used alone or in conjunction with one or more other such catalysts but in the absence of any metal salt catalyst of the kind previously proposed. In particular, acid catalysts of the invention offer the possibility of dispensing with
25 tin-based catalysts such as dibutyltin dilaurate.

The proportion of catalyst in a composition comprising components (A) and (B) may be in the range of from 0.01 to 5% by weight, advantageously from 0.05 to 2% by weight, and preferably not exceeding 1% by weight,
30 based on the total composition. For example, 0.01-1% by weight on solids of dibutyltin dilaurate may be added to the coating composition soon before application to the surface to be coated. With such a level of catalyst, the applied coating will typically cure tack-free within 1
35 day and be fully cured within 3-4 days.

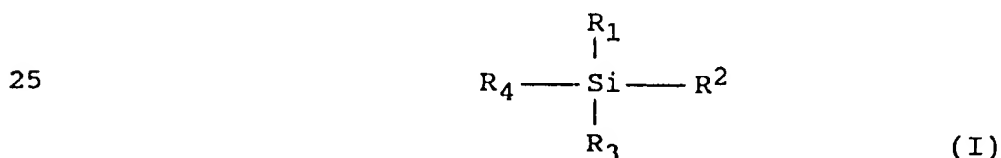
Depending upon the nature of the components (A) and

- 19 -

(B) and on the nature of the catalyst, it may be necessary for the catalyst to be packaged separately in a so-called "two-pack" system, or the catalyst may be packaged with one of the components but separately from the other.

As already indicated, it may be necessary or desirable to use a cross-linking agent for some or all of the curing reactions involved in the process of the invention. In addition to providing necessary functionality for cross-linking, the use of a cross-linking agent tends to lessen the extent to which there is a visible and mechanically removable layer of unreacted siloxane material at the outer surface of the applied coating. It has been observed (using ATR-FTIR spectroscopy) that the concentration of siloxane at the outer surface of a coating formed from a composition including a cross-linking agent is greater than the siloxane concentration at the outer surface (after removal of unreacted siloxane) of a coating formed from a composition having no cross-linking agent.

Advantageously, a cross-linking agent comprises a functional silane, more especially a functional silane of the formula

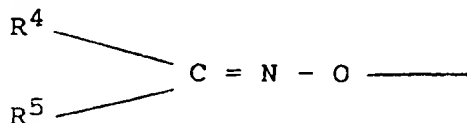


in which the groups represented by R^1 to R^4 may be the same or different and, subject to there being at least di-functionality, each may comprise a straight-chain or branched, saturated or unsaturated, aliphatic hydrocarbon radical, preferably having up to 7 carbon atoms, more especially up to 4 carbon atoms, or an aromatic or araliphatic hydrocarbon radical, such as, for example, phenyl or benzyl, or an aliphatic or aromatic ether group, such as an alkoxy, phenoxy or benzyloxy

- 20 -

group, or an ester group. An aliphatic group R^1 to R^4 is preferably an alkyl group, advantageously a C_1 - C_4 alkyl group, preferably a methyl or ethyl group, and an alkoxy group R^1 to R^4 is advantageously C_1 - C_4 alkoxy, preferably methoxy or ethoxy. Preferred examples of alkoxy-silanes of the formula (I) include tetraalkyl orthosilicates such as tetramethyl, -ethyl, -propyl or -butyl orthosilicate, dimethoxydimethyl silane and diethoxydimethyl silane. It will be appreciated that, in order to serve as a cross-linking agent, a compound of formula (I) must be at least difunctional and preferably at least tri-functional. Any of the groups R^1 to R^4 in formula (I) may be unsubstituted or may be substituted by one or more substituents selected, for example, from halogen (especially chlorine or fluorine), amino groups or alkyl groups, which may themselves be substituted or unsubstituted.

Alternatively, a functional silane cross-linking agent may be reactive by virtue of one or more oxime groups of the formula



in which R^4 and R^5 may be the same or different and each represents a straight-chain or branched saturated or unsaturated, aliphatic hydrocarbon radical, preferably having up to 7 carbon atoms, more especially up to 4 carbon atoms, especially a methyl or ethyl group; an aromatic group, for example, a phenyl group; or an araliphatic group, for example, a benzyl group, or R^4 and R^5 together represent an alkylene group, or one of R^4 and R^5 represents hydrogen. A group R^4 and/or R^5 may be substituted or unsubstituted.

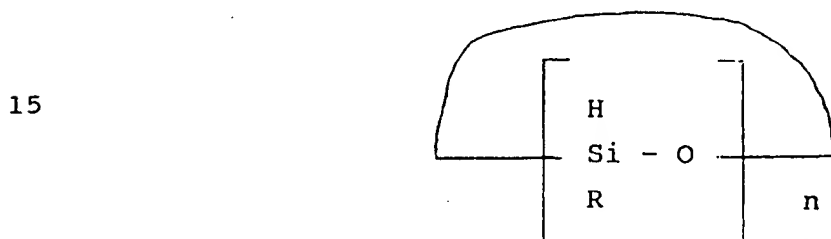
Thus, the functional silane may be a ketiminoxy-silane, for example, methyl tris(methylethylketiminoxy) silane, or one or more of the following ketiminoxy silanes:

- 21 -

- $\text{CH}_3\text{Si} [\text{ON} = \text{C}(\text{CH}_3)_2]_3$, $\text{CH}_3\text{Si} [\text{ON} = \text{C}(\text{CH}_3)\text{C}_2\text{H}_5]_3$,
 $(\text{CH}_2 = \text{CH})\text{Si} [\text{ON} = \text{C}(\text{CH}_3)\text{C}_2\text{H}_5]_3$, $\text{C}_6\text{H}_5\text{Si} [\text{ON} = \text{C}(\text{CH}_3)_2]_3$,
 $\text{CH}_3\text{Si} [\text{ON} = \text{C}(\text{C}_2\text{H}_5)(\text{CH}_2)_3\text{CH}_3]_3$,
 $(\text{CH}_3)_2\text{C} = \text{NOSi} [\text{ON} = \text{C}(\text{CH}_3)\text{C}_2\text{H}_5]_3$
 5 $\text{CH}_3\text{Si} [\text{ON} = \text{C}(\text{CH}_2)_4]_3$,
 $\text{CH}_3\text{Si} [\text{ON} = \text{C}(\text{CH}_2)_5]_3$,
 $\text{Si}[\text{ON} = \text{C}(\text{C}_2\text{H}_5)(\text{CH}_3)]_4$ or $\text{Si}[\text{ON} = \text{C}(\text{CH}_3)_2]_4$.

Other possible cross-linking or curing agents include oximes such as vinyltris(methylethylketoxime) or
 10 methyltris(methylethylketoxime).

As a further possibility, more particularly when organometallic catalysts are used, especially tin-based catalysts, a cross-linking or curing agent may comprise a cyclic compound of the following formula:



in which n is an integer of from 3 to 10, and R represents hydrogen or methyl.

20 A silane cross-linking agent may in principle be incorporated in a monomeric form or in the form of a self-condensation product, which may be, for example, a dimer, trimer, heptamer or a low molecular weight polymer.

25 Advantageously, especially when the cross-linking agent is a functional silane, the proportion of cross-linking agent in the composition comprising components (A) and (B) may be in the range of from 0.05 to 10% by weight, generally from 2 to 5% by weight, based on the
 30 weight of component (B) in the composition.

It has been found that compositions which comprise a polymer (A) which does not contain silanol groups and a poly(diorganosiloxane) (B) which does contain silanol

groups are stable on storage provided that the polymer (A) does not contain groups known to be effective as catalysts in curing silicones, for example amines and the metal salts of carboxylic acids as mentioned above. It has further been found that compositions containing no silanol groups but containing groups effective as catalysts are stable in the absence of moisture.

The process for forming the initial coating from the composition comprising components (A) and (B) is most conveniently carried out using a solution of the composition in a non-reacting volatile solvent for the composition. Suitable solvents include aromatic hydrocarbons, for example toluene, xylene and trimethylbenzene; alcohols, for example, butanol; ketones, for example 4-methylpentan-2-one (methylisobutylketone), 5-methylhexan-2-one (methylisoamylketone) and cyclohexanone; esters, for example butyl acetate and 2-ethoxyethyl acetate, and mixtures of the above with one another or with an aliphatic hydrocarbon, for example in the form of white spirit. Such solutions can be applied to the surface to be coated by any of the known methods such as brush-painting, roller-painting, spray-painting and using aerosol formulations. In order to minimise the use of solvent on both cost and environmental grounds, it is advantageous to use as concentrated a solution as possible which is compatible with the coating technique employed. A solution of the coating composition comprising components (A) and (B) may comprise at least 35% by weight solids, generally at least 50% by weight solids. More concentrated solutions, for example containing at least 70% solids, may be employed if the polymer component (A) is of low molecular weight. In principle, the maximum solids content may be as high as 90% by weight or even more, but in general the maximum practicable solids content will be in the range 75-85% by weight, typically 80% by weight.

For condensation cure, the coating compositions comprising components (A) and (B) of the present invention require the presence of water in order to achieve full cure, but specific addition of water is not
5 normally required, either during or after application of the composition. It has been found that atmospheric moisture or the water commonly found on damp surfaces to be coated is sufficient to induce curing, and it will not normally be necessary or appropriate to heat the applied
10 coating for curing purposes.

Because compositions comprising components (A) and (B) are in general sensitive to the presence of water, it is preferable to take steps to minimise the water content of all ingredients of the composition, and it will be
15 appreciated that no water or aqueous material should be added. Thus, for example, commercially available solvents will frequently contain a small amount of water (say, 1-2% by volume) and it is preferable to reduce the water content of such materials before use. In
20 principle, such reduction in water content may be achieved by distillation in conjunction with a drying agent such as, for example, sodium, sodium hydride or calcium hydride or anhydrous calcium sulphate, but advantageously a reactive water-scavenger is used, for
25 example, an inorganic salt such as, for example, magnesium sulphate (followed by filtration) or a mono- or di-functional silane, for instance, ethoxytrimethyl silane.

Compositions comprising components (A) and (B) and
30 the coatings derived therefrom may also include one or more unreactive oils such as, for example, a silicone oil, especially a methyl phenylsilicone oil such as that sold by Rhone-Poulenc under the trademark "Rhodorsil Huile 550" or a petroleum or polyolefin oil or a
35 polyaromatic oil.

It has proved to be especially advantageous, in

- 24 -

terms of the enrichment of the outermost surface region of the applied coating with siloxane material (in some cases leading to the formation of a morphologically distinct outermost layer comprising siloxane material) for the composition to include a quantity of a petrolatum oil. In the case of coatings formed from a composition not including petrolatum, there may in some cases be a very thin layer of pure siloxane component at the outer surface, with a siloxane-rich layer underneath. In the case of a coating formed from the same composition but including petrolatum, a relatively thick siloxane-rich layer is formed, typically at least an order of magnitude thicker than the siloxane-rich layer formed without the use of petrolatum; such a siloxane-rich layer may comprise a 50/50 mixture of siloxane and petrolatum.

The proportion of petrolatum is advantageously in the range of from 5 to 25% by weight (based on the amount of component (A) preferably in the range of from 15 to 20% by weight. The proportion of petrolatum oil used may be higher than 25% by weight, but proportions above 25% by weight in unpigmented systems will in general lead to an undesirable decrease in the integrity of the applied coating. In the case of pigmented systems it may be possible to use a proportion of petrolatum oil above 25% by weight, possibly as high as 30% or 35% by weight.

If desired, a petrolatum oil may be used in conjunction with another unreactive oil such as an aromatic hydrocarbon oil or oils (AHO), or any of the other unreactive oils specifically mentioned hereinbefore.

The compositions comprising components (A) and (B) can be pigmented, for example at a pigment volume concentration of 0.5 to 25%, or dyed, or can be used as clear transparent coatings.

The compositions may also contain other excipients and/or fillers such as barium sulphate or other mineral fillers, pyrogenic silica, bentonite or other clays,

- 25 -

typically in a proportion of from 0.5 to 5% by weight, preferably from 1 to 2% by weight.

The coating compositions comprising components (A) and (B) can be single-pack coatings for moisture cure, or
 5 a two-pack system may be used. Thus, for example, the polymer component (A) can be packaged separately from the polysiloxane (B), and any catalyst is preferably packaged separately from the polymer component (A).

Examples of possible two-pack systems are as follows:

10	(a)	<u>Pack I</u>	<u>Pack II</u>
		Component (A)	Cross-linking agent
		Component (B)	Catalyst
		Pigment	Solvent
		Filler	
15		Solvent	
	(b)	<u>Pack I</u>	<u>Pack II</u>
		Component (A)	Component (B)
		Pigment	Cross-linking agent
		Filler	Catalyst
20		Solvent	Solvent

In relation to the following aspects, the discussion above in connection with component (B) is in principle also applicable to (C):

- 25 (a) Chemical constitution, including the nature of the curable functional groups;
- (b) Use of catalyst;
- (c) Use of cross-linking agent;
- (d) Molecular weight;
- (e) Viscosity;
- 30 (f) Mode of application, including solvent usage and the solids content of an application solution;
- (g) Optional use of unreactive oil(s); and
- (h) Optional use of pigments.

35 The following technical considerations may be mentioned in particular:

- 26 -

- i) Silanol functionality is preferred, but alkoxy functionality may also be advantageous.
- ii) The viscosity of component (C) may be in the range of from 1 to 200 poise at 25°C., but is preferably from 20 to 50 poise, more especially from 35 to 50 poise.
- iii) Use of a tin catalyst is preferred for the curing of component (C) - in terms of the cure profile for the reaction - but may in some cases be less favoured for the (A)/(B) curing reaction, especially if aminofunctionality is present.
- iv) Use of an acid catalyst may be less preferred in the curing of component (C).
- v) The use of pigments and other excipients and/or fillers does not in general lead to any difficulties in relation to component (C), and may be advantageous not only in terms of the appearance of the outer coating but also in facilitating the application of relatively thick layers. In terms of visual appearance, the use of such materials may be dispensed with in the composition comprising components (A) and (B) if the layer (C) is to be applied directly to the freshly-prepared coating formed therefrom, and in any event it may be found that the use of pigments or other excipients and/or fillers may interfere with optimum surface layer constitution as described hereinbefore.

Preferably, for optimum compatibility of the layer derived from (C) with the cured coating derived from (A) and (B), component (C) is similar to or substantially identical with component (B) of the initial coating composition, especially in terms of one or more and preferably all of features (a)-(e) above.

Depending on reactivities, a composition comprising (C) can in principle be packaged in a one-, two- or three-pack system.

The thickness of the coating formed by curing of the

- 27 -

composition comprising components (A) and (B) may be in the range of from 50 to 100 microns, and the thickness of the layer comprising cured component (C) will typically be in the same range. More than one layer (C) can be applied if desired.

The following Examples illustrate one-, two- and three-pack compositions for forming the outermost layer derived from component (C), of a fouling-inhibiting coating in accordance with the invention. All viscosity data are at 25°C.:

Example 1: One-pack composition

	<u>Parts by weight</u>
$\alpha\omega$ -hydroxy functional dimethyl siloxane (viscosity 200 poise)	20.00
15 Methyltrimethoxy silane	2.00
Xylene	15.00
Tetrabutyltitanate	0.30

Example 2: One-pack composition

	<u>Parts by weight</u>
20 $\alpha\omega$ -hydroxy functional dimethyl siloxane (viscosity 200 poise)	20.00
$\alpha\omega$ -hydroxy functional dimethyl siloxane (viscosity 7.5 poise)	5.00
Methyltrimethoxy silane	2.00
25 Xylene	15.00
Tetrabutyltitanate	0.30

Example 3: One-pack composition

	<u>Parts by weight</u>
$\alpha\omega$ -hydroxy functional dimethyl 30 siloxane (viscosity 35 poise)	55.00
Methyltrimethoxy silane	2.50
Airflow silica (Aerosil)	2.20
Titanium ethylacetoacetate	1.00
Trimethylbenzenes	29.40

Example 4: Three-pack compositionParts by weightBase

	$\alpha\omega$ -hydroxy functional dimethyl	
5	siloxane (viscosity 35 poise)	56.00
	Air floated silica (Aerosil)	1.70
	Silicone oil (Rhodorsil RP550)	4.10
	Trimethylbenzenes	11.10

Curing agent

10	Tetraethylorthosilicate	2.60
	Silicone oil (Rhodorsil RP550)	0.80
	Trimethylbenzenes	8.50

Catalyst Solution

	Dibutyltindilaurate	0.55
15	Trimethylbenzenes	14.20

Example 5: Three-pack compositionParts by weightBase

	$\alpha\omega$ -hydroxy functional dimethyl	
20	siloxane (viscosity 35 poise)	65.74
	Air floated silica (Aerosil)	2.03
	Silicone oil (Rhodorsil RP550)	0.47
	Petrolatum (hydrocarbon wax)	3.59
	Trimethylbenzenes	11.10

25 Curing agent

	Tetraethylorthosilicate	3.00
	Silicone oil (Rhodorsil RP550)	0.90

Catalyst Solution

	Dibutyltindilaurate	1.29
30	Trimethylbenzenes	9.93

Example 6: Three-pack compositionParts by weightBase

	$\alpha\omega$ -hydroxy functional dimethyl	
5	siloxane (viscosity 35 poise)	55.60
	Air floated silica (Aerosil)	1.35
	Titanium dioxide	13.23
	Trimethylbenzenes	7.77

Curing agent

10	Tetraethylorthosilicate	2.56
	Silicone oil (Rhodorsil RP550)	4.95
	Trimethylbenzenes	9.98

Catalyst Solution

	Dibutyltindilaurate	0.46
15	2,4-pentanedione (retards catalyst)	4.10

Example 7: Three-pack compositionParts by weightBase

	$\alpha\omega$ -hydroxy functional dimethyl	
20	siloxane (viscosity 35 poise)	55.40
	Air floated silica (Aerosil)	1.37
	Sicomine yellow (L1622U)	13.60
	Trimethylbenzenes	7.75

Curing agent

25	Tetraethylorthosilicate	2.54
	Silicone oil (Rhodorsil RP550)	4.90
	Trimethylbenzenes	9.88

Catalyst Solution

	Dibutyltindilaurate	0.45
30	2,4-pentanedione (retards catalyst)	4.06

Example 8: Three-pack composition

		<u>Parts by weight</u>
<u>Base</u>		
	$\alpha\omega$ -hydroxy functional dimethyl	
5	siloxane (viscosity 25 poise)	55.60
	Air floated silica (Aerosil)	1.35
	Trimethylbenzenes	7.77
<u>Curing agent</u>		
	Tetraethylorthosilicate	2.50
10	Trimethylbenzenes	7.88
<u>Catalyst Solution</u>		
	Dibutyltindilaurate	0.50
	Trimethylbenzenes	2.35

Example 9: Three-pack composition

		<u>Parts by weight</u>
<u>Base</u>		
	$\alpha\omega$ -methoxy functional dimethyl	
	siloxane (viscosity 10 poise)	55.60
	Air floated silica (Aerosil)	1.35
20	Trimethylbenzenes	7.77
<u>Curing agent</u>		
	Tetraethylorthosilicate	2.50
	Trimethylbenzenes	7.88
<u>Catalyst Solution</u>		
25	Dibutyltindilaurate	0.50
	Trimethylbenzenes	2.35

Example 10: Three-pack compositionParts by weightBase

	$\alpha\omega$ -hydroxy functional dimethyl	
5	siloxane (viscosity 35 poise)	56.26
	Air floated silica (Aerosil)	1.74
	Silicone oil (Rhodorsil RP550)	4.13
	Trimethylbenzenes	11.17

Curing agent

10	Tetraethylorthosilicate	2.57
	Silicone oil (Rhodorsil RP550)	0.77
	Trimethylbenzenes	8.50

Catalyst Solution

	bis (2-ethylhexyl) hydrogen phosphate	2.50
15	Trimethylbenzenes	13.36

Example 11: Three-pack compositionParts by weightBase

	$\alpha\omega$ -hydroxy functional dimethyl	
20	siloxane (viscosity 35 poise)	55.60
	Air floated silica (Aerosil)	1.35
	Titanium dioxide	13.23
	Trimethylbenzenes	7.77

Curing agent

25	Tetraethylorthosilicate	2.56
	Silicone oil (Rhodorsil RP550)	4.95
	Trimethylbenzenes	9.98

Catalyst Solution

	bis (2-ethylhexyl) hydrogen phosphate	2.52
30	Trimethylbenzenes	2.03

Example 12: Two-pack compositionParts by weightBase

	$\alpha\omega$ -hydroxy functional dimethyl	
5	siloxane (viscosity 35 poise)	100.00
	Air floated silica (Aerosil)	8.00
	Methyltris(methylethylketoxime)silane	6.00

Catalyst Solution

	Trimethylbenzenes	15.00
10	Dibutyltindilaurate	0.08

CLAIMS

- 1) A process for inhibiting fouling of a substrate in a fouling environment, which comprises applying to the substrate, before exposure to the said environment, a composition which comprises:
- (A) a polymer carrying pendant and/or terminal curable functional groups, at least a major proportion of the repeating units in the polymer of (A) being other than siloxane units,
- (B) one or more polysiloxanes having pendant and/or terminal curable functional groups and selected from curable organohydrogen polysiloxanes and curable polydiorganosiloxanes, the curable functional groups in component (B) being capable of undergoing a curing reaction with the curable functional groups in component (A),
- and curing the applied composition comprising components (A) and (B), if necessary or desired in conjunction with a cross-linking agent,
- and thereafter applying a layer comprising
- (C) a curable organohydrogen polysiloxane or polydiorganosiloxane,
- and curing the applied layer, if necessary or desired in conjunction with a cross-linking agent.
2. A process as claimed in claim 1, wherein the curable layer (C) is applied to a freshly-prepared coating formed by curing the composition comprising components (A) and (B).
3. A process as claimed in claim 1, wherein the curable layer (C) is applied to a coating formed by curing the composition comprising components (A) and (B), which coating has been worn and/or damaged in use.
4. A process as claimed in claim 1, wherein component (A) comprises pendant curable functional groups.

- 34 -

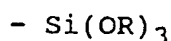
5. A process as claimed in any one of claims 1 to 4, wherein component (A) comprises curable silicon-containing functional groups.

6. A process as claimed in any one of claims 1 to 5, wherein the polymer of (A) is derived from one or more monomers (A1) which carry curable silicon-containing groups and one or more monomers (A2) which do not carry such groups.

7. A process as claimed in claim 6, wherein the monomer(s) (A1) carry pendant curable silicon-containing groups and the molar proportion of monomer(s) (A1) to that of monomers (A2) is in the range of from 1% to 50%.

8. A process as claimed in any one of claims 1 to 7, wherein curable silicon-containing groups in component (A) are curable by virtue of one or more curable functional groups selected from aliphatic, aromatic and araliphatic ether, ester and oxime groups, which groups may be substituted or unsubstituted.

9. A process as claimed in claim 8, wherein curable silicon-containing groups in component (A) are of the formula



wherein R is a straight-chain or branched alkyl group having from 1 to 4 carbon atoms.

10. A process as claimed in any one of claims 1 to 8, wherein curable silicon-containing groups in component (A) are other than trihydroxysilyl groups.

11. A process as claimed in any one of claims 1 to 10, wherein substantially all of the curable functional groups in component (A) are silicon-containing groups.

12. A process as claimed in any one of claims 1 to 11, wherein the proportion of siloxane repeating units in component (A) does not exceed 25%.

13. A process as claimed in claim 12, wherein component (A) is substantially free from siloxane repeating units.

- 35 -

14. A process as claimed in any one of claims 1 to 13 wherein the polymer of component (A) is derived from one or more ethylenically unsaturated monomers.

15. A process as claimed in any one of claims 1 to 14, wherein the curable polysiloxane (B) is curable by virtue of silanol groups.

16. A process as claimed in any one of claims 1 to 14, wherein the curable polysiloxane (B) is curable by virtue of silicon-containing groups.

17. A process as claimed in any one of claims 1 to 14, wherein the curable polysiloxane (B) is curable by virtue of curable functional groups selected from aliphatic, aromatic and araliphatic ether, ester and oxime groups, trialkoxysilyl or hydrosilyl groups.

18. A process as claimed in any one of claims 1 to 17, wherein component (B) does not contain any amino functionality.

19. A process as claimed in any one of claims 1 to 18, wherein some or all of the curable functional groups in component (B) are bonded directly to silicon.

20. A process as claimed in any one of claims 1 to 19, wherein component (B) comprises a linear polymer.

21. A process as claimed in claim 20, wherein component (B) has the structure $R^3O(SiR^1R^2O)_nR^3$, in which R^1 and R^2 , which may be the same or different on each silicon atom and on different silicon atoms in the polymer, each represents an alkyl group; an alkenyl group; a cycloalkyl or cycloalkenyl group; an aryl group; or a halogenated or cyano-substituted hydrocarbon group, with the proviso that one of R^1 and R^2 may represent hydrogen on some or all of the silicon atoms and that R^1 and R^2 may each represent hydrogen on some of the silicon atoms, OR^3 represents a curable functional group in which R^3 represents a monovalent radical, and n represents a degree of polymerisation.

- 36 -

21. A process as claimed in any one of claims 1 to 20, wherein component (B) has a number-average molecular weight in the range of from 5000 to 85000.

22. A process as claimed in any one of claims 1 to 5 21, wherein the or each cross-linking agent comprises a functional silane.

23. A process as claimed in any one of claims 1 to 22, wherein the composition comprising components (A) and (B) includes one or more unreactive oils selected 10 from silicone oils, petroleum oils, polyolefin oils, and polyaromatic oils.

24. A process as claimed in any one of claims 1 to 23, wherein the composition comprising components (A) and (B) includes a catalyst for the curing reaction.

15 25. A process as claimed in any one of claims 1 to 24, wherein the proportion of component (A) is in the range of from 50% to 99% by weight, and the proportion of component (B) is in the range of from 1 to 50% by weight, the percentages being based on the total weight 20 of (A) + (B).

26. A process as claimed in any one of claims 1 to 25, wherein the proportion of component (B) is at least 5% by weight, based on the total weight of (A) + (B).

27. A process as claimed in any one of claims 1 to 25 26, wherein the polysiloxane (C) is a material as specified in any one of claims 15 to 21.

28. A process as claimed in any one of claims 1 to 27, wherein the polysiloxane (C) is curable by virtue of silanol or silicon-alkoxy groups.

30 29. A process as claimed in any one of claims 1 to 28, wherein the applied layer comprising (C) includes a catalyst for the curing of that layer.

30. A process as claimed in claim 29, wherein the catalyst for the curing of the layer comprising (C) is a 35 tin catalyst.

31. A process as claimed in any one of claims 1 to

- 37 -

30, wherein the applied layer comprising (C) includes an unreactive oil or wax.

32. A process as claimed in any one of claims 1 to 31, wherein the thickness of the coating formed by curing
5 of the composition comprising components (A) and (B) is in the range of from 50 to 100 microns.

33. A process as claimed in any one of claims 1 to 32, wherein the thickness of the layer comprising cured component (C) is in the range of from 50 to 100 microns.

10 34. A process as claimed in any one of claims 1 to 33, in which the substrate is pre-treated with an anti-corrosive material.

35. A process as claimed in any one of claims 1 to 34, wherein the fouling environment is an aquatic
15 environment.

36. A process as claimed in claim 35, wherein the fouling environment is a marine environment.

37. A substrate in a fouling environment and bearing a coating formed as defined in any one of claims
20 1 to 36.

INTERNATIONAL SEARCH REPORT

Inter. Application No

PCT/GB 98/00706

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09D5/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 93 13179 A (COURTAULDS COATINGS) 8 July 1993 cited in the application see claims ---	1-37
Y	GB 2 300 370 A (GENERAL ELECTRIC COMPANY) 6 November 1996 see page 2, line 28 - page 3, line 19 see page 4, paragraph 3 see page 5, line 7-8 see page 7, paragraph 3 ---	1-37
A	EP 0 089 066 A (WACKER-CHEMIE) 21 September 1983 see claim 1; example 2 --- -/--	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

16 June 1998

Date of mailing of the international search report

25/06/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Girard, Y

INTERNATIONAL SEARCH REPORT

Interr. nal Application No

PCT/GB 98/00706

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 032 597 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ) 29 July 1981 see abstract see page 9, line 30-32 ---	1
A	EP 0 532 273 A (COURTAULDS COATINGS) 17 March 1993 see abstract see page 5, line 44-47 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 98/00706

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9313179 A	08-07-1993	AU 3168193 A	28-07-1993
		CA 2126233 A	08-07-1993
		EP 0617725 A	05-10-1994
		GB 2277093 A, B	19-10-1994
		JP 7506599 T	20-07-1995
		NO 942305 A	17-06-1994
		NZ 246197 A	25-06-1996
		US 5663215 A	02-09-1997
GB 2300370 A	06-11-1996	US 5691019 A	25-11-1997
		DE 19606966 A	07-11-1996
		FR 2733761 A	08-11-1996
		JP 8318217 A	03-12-1996
EP 89066 A	21-09-1983	DE 3209755 A	22-09-1983
		CA 1183412 A	05-03-1985
		DK 112283 A	18-09-1983
		JP 58166967 A	03-10-1983
		US 4431472 A	14-02-1984
EP 32597 A	29-07-1981	DK 524780 A, B,	12-06-1981
		JP 1496697 C	16-05-1989
		JP 56092971 A	28-07-1981
		JP 63042675 B	24-08-1988
EP 532273 A	17-03-1993	US 5192603 A	09-03-1993
		WO 9306180 A	01-04-1993